DRAFT

METHIDATHION

RISK CHARACTERIZATION DOCUMENT

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Environmental Fate

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ENVIRONMENTAL FATE OF METHIDATHION

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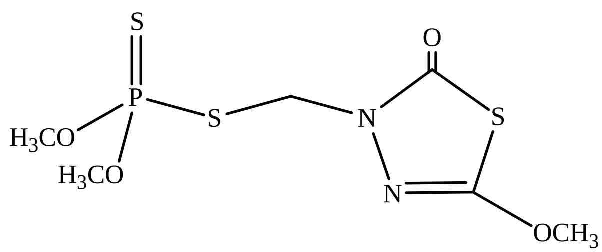
ENVIRONMENTAL FATE OF METHIDATHION

Chemical Description



Chemical Name (CA)	S-[(5-methoxy-2oxo-1,3 4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl phosphoro-dithioate
Common Name	Methidathion
CAS Registry Number	950-37-8
Molecular Formula	$C_6H_{11}N_2O_4PS_3$
Molecular Weight	302.33
Chemical Family	Organophosphorus; thiadizole

Methidathion is a colorless crystal belonging to the chemical family of organophosphates (sub-class phosphorodithioates). It is sparingly soluble in water and readily soluble in common organic solvents such as ethanol, benzene, methanol, and acetone. Methidathion is hydrolyzed in alkaline and strongly acidic media, and is relatively stable to hydrolysis in neutral and slightly acidic media (British Crop Protection Council. 2003; O'Neil, 2001). Additional physical and chemical properties are summarized in Table 1. Wildlife toxicity data are summarized in Table 2.

Table 1. Physical and chemical properties of methidathion (DPR, 2005a; British Crop Protection Council, 2003).

Physical/Chemical Property	Value
Melting point	39.9 °C
Vapor Pressure	3.37×10^{-6} mm Hg (25 °C)
Water Solubility	221 ppm (22 °C, pH 4.4)
Henry's Law Constant (K_h)	1.95×10^{-9} atm-m^3-mol
Octanol-water Partition Coefficient (K_{ow})	166

Table 2. Wildlife toxicity of methidathion (Menconi & Siepmann, 1996; U.S. Environmental Protection Agency, 1999).

Species	Test	Toxicity
Mallard duck	14-day LD_{50}	23.6 mg/kg
Rainbow trout	96-hour LC_{50}	10.5 μg/L
Bluegill sunfish	96-hour LC_{50}	17.2 μg/L
Honeybee	48-hour LD_{50}	0.23 μg/bee
Mysid shrimp	96-hour LC_{50}	0.7 μg/L
Daphnia magna	48-hour LC_{50}	7.2 μg/L

Regulation

Methidathion has been classified as a federally restricted use pesticide due to its high acute oral toxicity (U.S. Environmental Protection Agency, 1999). Consequently, it was designated a restricted material pursuant to section 14005.5 of the Food and Agricultural Code. Other criteria for a restricted material designation in this section include posing a danger to public health, or a hazard to crops, domestic animals, farm workers, or the environment. Restricted materials are possessed and used by persons only under permit of the county agricultural commissioner.

The Birth Defect Prevention Act (Stats. 1984, Ch. 669, § 1) mandates the listing of methidathion in section 6198.5 of Title 3, California Code of Regulations. The 200 priority pesticide active ingredients listed in this section are suspected of being hazardous to people, and have widespread use and significant data gaps. All data requirements for methidathion have been submitted to the Department of Pesticide Regulation (DPR).

Use Profile

Methidathion is a non-systemic insecticide/acaricide used to control sucking and chewing insects for a wide variety of crops. It is available in emulsifiable concentrate and soluble powder formulations, which have the signal word "Danger/Poison" on the product labels. It is also available in a soluble powder formulation, which has the signal word "Warning" on the product label. As of June 28, 2005, there were three active registrations for products containing methidathion (DPR, 2005b)

Methidathion is applied by aerial or calibrated power-operated ground spray equipment. Application rates are summarized in Table 3.

Table 3: Summary of methidathion application rates in pounds of active ingredient per acre.

Commodity	[a]Rates
Almonds; Deciduous Fruits	0.75 – 3
Artichokes	1.0
Citrus Fruits	5.0
Cotton	0.25 – 1.0
Mangoes	0.25 – 0.5
Olives	2.0
Safflowers; Sunflowers	0.5
Walnuts	1.0 – 2.0

[a] concentrated sprays

Full pesticide use reporting in California was implemented by DPR in 1990. All agricultural use must be reported monthly to the county agricultural commissioners. The county agricultural commissioners forward these data to DPR, who annually compiles and makes available a pesticide use report. Agricultural use is defined as including applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way. Although use in structural pest control is excluded from the definition, the use of pesticides designated as restricted materials pursuant to section 14005.5 of the Food and Agricultural Code must be reported. For non-agricultural applications, detailed information such as base meridian/township/range/section is not provided.

Figure 1 is a graphical representation of total pounds of methidathion used in California in 1991 and from 1994 through 2003. Total use ranged from 370,087 pounds in 1994 to 54,398 pounds in 2003. The average annual use for the ten-year reporting period was 198,575 pounds. Table 4 and Figure 2 show use by county in 1991 and from 1994 through 2003 for counties where ten-year average use exceeded 60,000 pounds. Table 5 and Figure 3 show monthly use in 1991 and from 1994 through 2003. Table 6 and Figure 4 show methidathion use by commodity/site in 1991 and from 1994 through 2003 for commodities where ten-year average use exceeded 100,000 pounds (DPR PUR Database).

Figure 1. Methidathion reported use in 1991 and from 1994 through 2003 (DPR PUR Database).

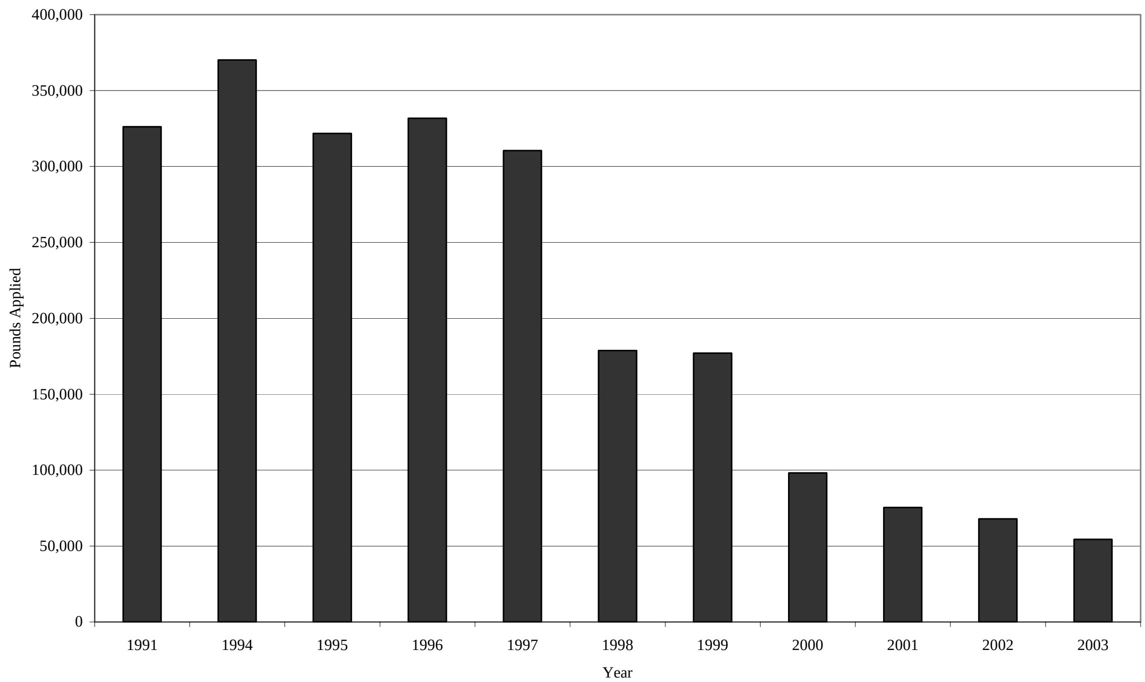


Table 4. Methidathion use by county in 1991 and from 1994 through 2003 for counties where ten-year average use exceeded 60,000 pounds (DPR PUR Database).

	Pounds Applied										
County	**1991**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
BUTTE	12,029	18,973	17,041	19,417	17,232	10,451	4,105	1,845	2,060	1,245	875
FRESNO	37,117	57,658	48,841	38,599	54,073	23,773	21,740	8,305	10,611	8,628	5,881
KERN	21,994	61,333	59,625	58,300	63,855	35,901	47,145	25,340	26,722	14,048	14,128
KINGS	34,557	16,456	17,159	16,729	8,725	5,313	3,757	1,405	1,710	955	1,455
MONTEREY	17,867	18,743	15,070	18,147	14,581	14,581	14,950	15,271	14,220	11,903	4,851
SAN JOAQUIN	18,588	18,321	10,931	13,597	13,830	11,499	7,988	6,023	4,743	3,489	3,374
STANISLAUS	33,797	18,428	10,284	17,167	8,743	9,236	6,474	5,274	2,557	1,075	2,973
SUTTER	17,954	14,296	13,702	19,150	12,444	9,034	2,981	8,012	3,675	2,704	1,969
TULARE	75,582	103,008	82,379	86,966	73,097	34,695	50,483	14,630	15,857	16,736	9,518

Figure 2. Methidathion use by county in 1991 and from 1994 through 2003 for counties where ten-year average use exceeded 60,000 pounds (DPR PUR Database).

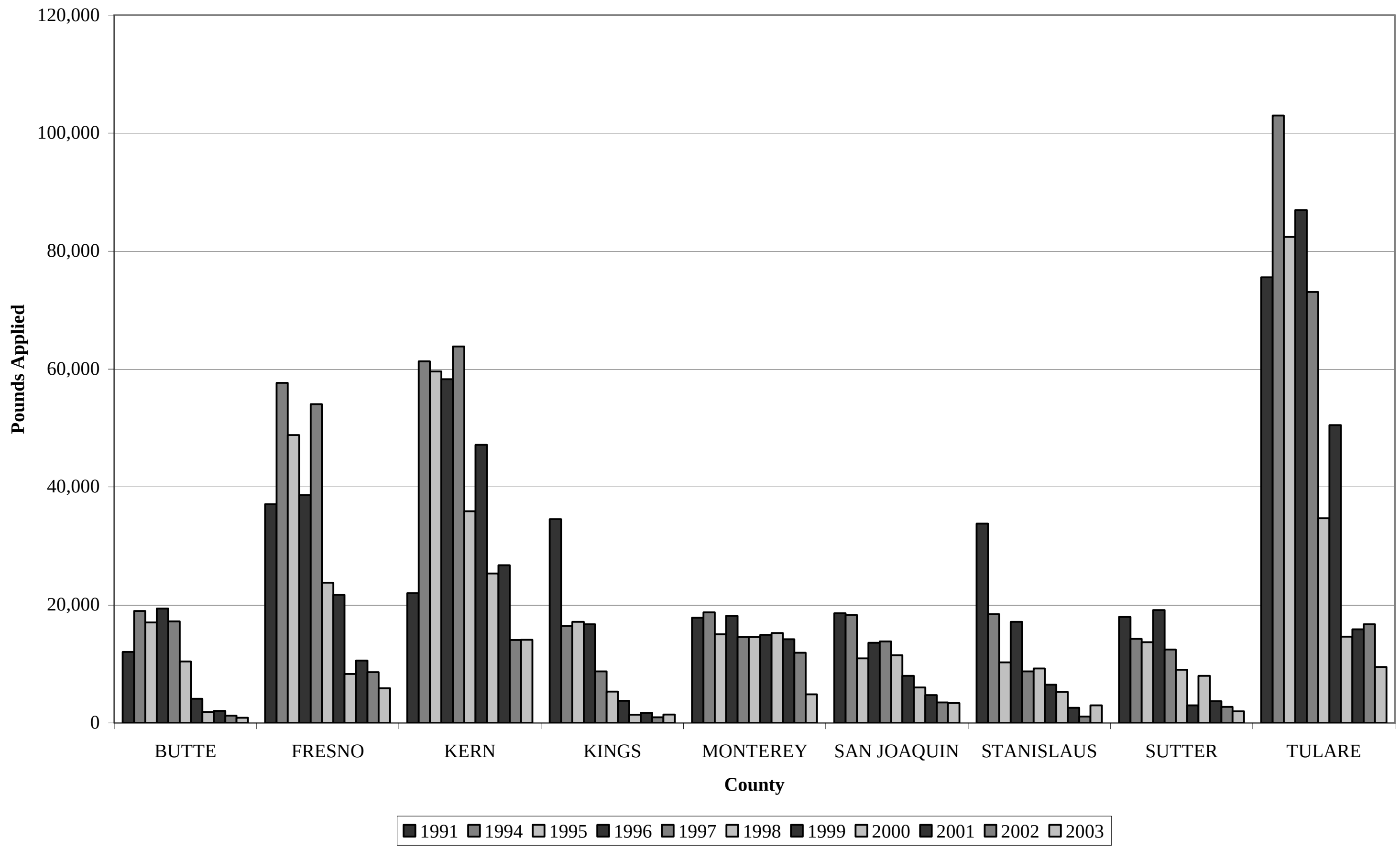


Table 5. Methidathion use by month in 1991 and from 1994 through 2003 (DPR PUR Database).

	Pounds Applied										
Month	1991	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
JAN	109,978	153,786	90,534	118,038	110,277	76,851	70,346	43,098	38,718	21,024	19,816
FEB	36,301	32,723	58,792	35,331	28,978	14,580	22,314	12,418	9,269	8,990	4,934
MAR	6,687	3,347	1,343	5,541	3,434	5,266	1,951	3,332	2,757	1,953	2,142
APR	10,434	3,419	2,074	2,588	8,923	317	628	1,416	466	342	383
MAY	16,318	20,592	13,558	32,686	36,246	6,136	3,679	2,722	1,388	3,621	2,194
JUN	68,032	71,455	53,025	47,111	21,851	18,945	21,505	9,066	11,046	11,915	5,338
JUL	30,172	28,441	42,404	48,690	34,901	16,624	20,096	10,028	14,613	9,710	4,360
AUG	15,126	11,045	18,896	10,898	7,605	9,785	12,394	2,448	4,940	1,910	7,705
SEP	8,424	6,567	7,604	6,480	4,215	3,384	4,410	870	2,889	962	2,008
OCT	5,686	7,618	9,669	2,702	10,123	3,432	4,407	1,241	2,224	2,673	2,307
NOV	1,391	2,300	4,430	3,938	2,246	1,688	4,651	620	2,436	2,316	1,741
DEC	17,630	28,795	19,421	17,783	41,673	21,742	10,693	10,870	2,776	2,972	1,749

Figure 3. Methidathion use by month in 1991 and from 1994 through 2003 (DPR PUR Database).

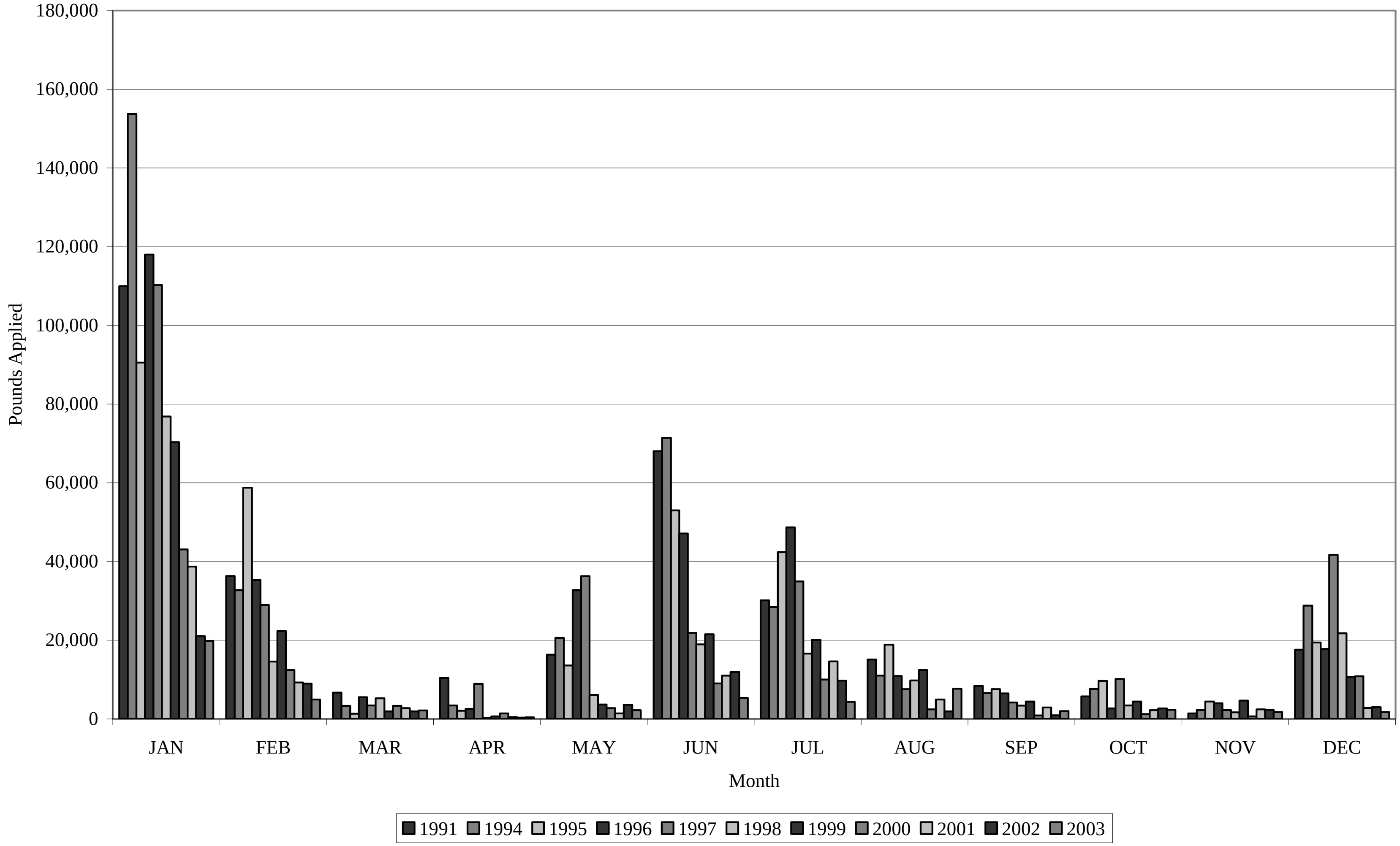
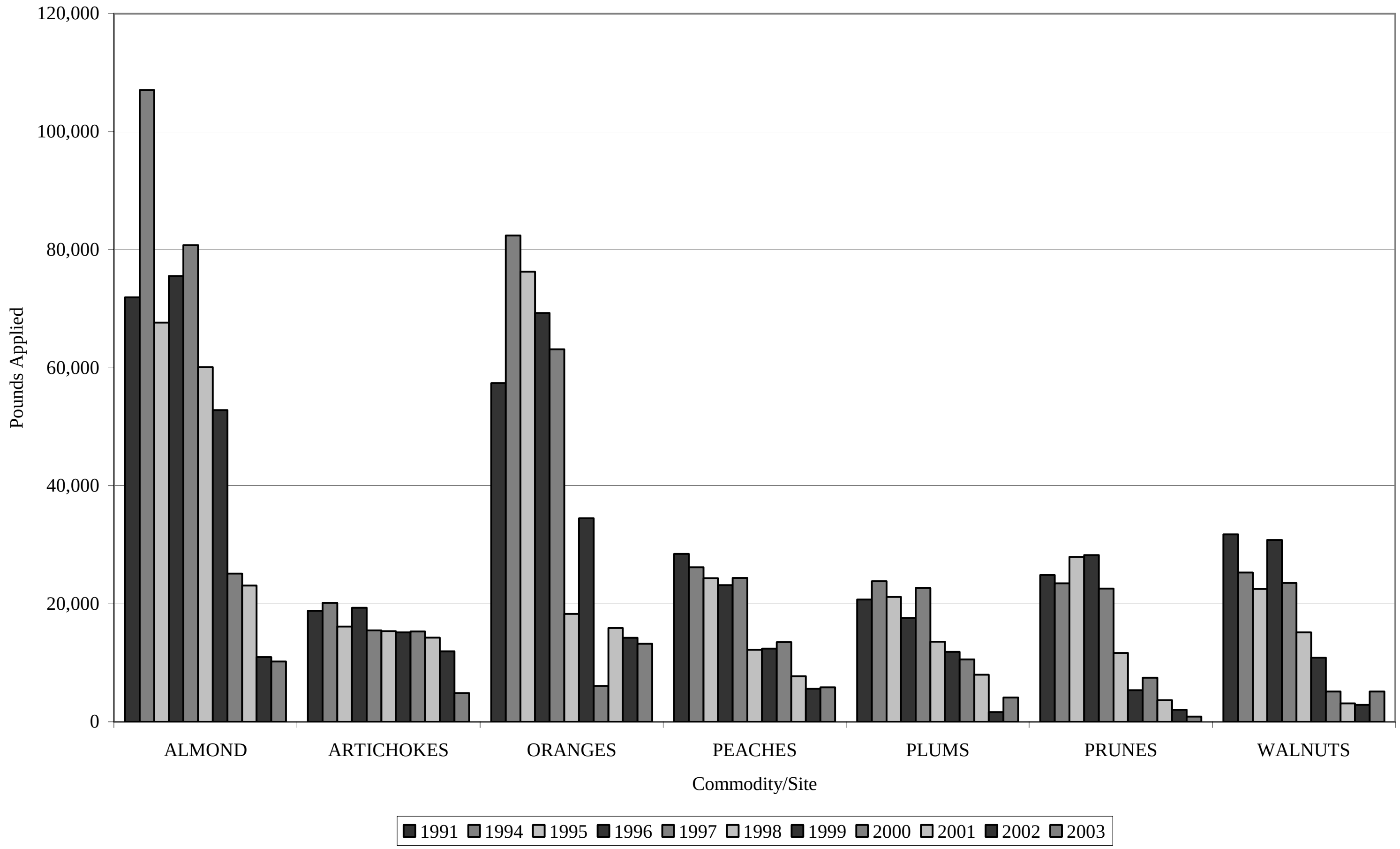


Table 6. Methidathion use by commodity/site in 1991 and from 1994 through 2003 for commodities where ten-year average use exceeded 100,000 pounds (DPR PUR Database).

	Pounds Applied										
Commodity/Site	**1991**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
ALMOND	71,907	107,060	67,645	75,516	80,791	60,115	52,820	25,120	23,105	10,974	10,216
ARTICHOKES	18,825	20,130	16,146	19,325	15,460	15,336	15,169	15,331	14,285	11,920	4,871
ORANGES	57,362	82,407	76,283	69,256	63,123	18,279	34,480	6,083	15,909	14,243	13,200
PEACHES	28,450	26,201	24,320	23,178	24,364	12,225	12,387	13,504	7,724	5,605	5,823
PLUMS	20,736	23,823	21,142	17,582	22,643	13,549	11,838	10,568	7,981	1,635	4,136
PRUNES	24,863	23,484	27,950	28,263	22,600	11,655	5,381	7,454	3,668	2,073	912
WALNUTS	31,741	25,315	22,503	30,812	23,526	15,162	10,899	5,130	3,115	2,879	5,138

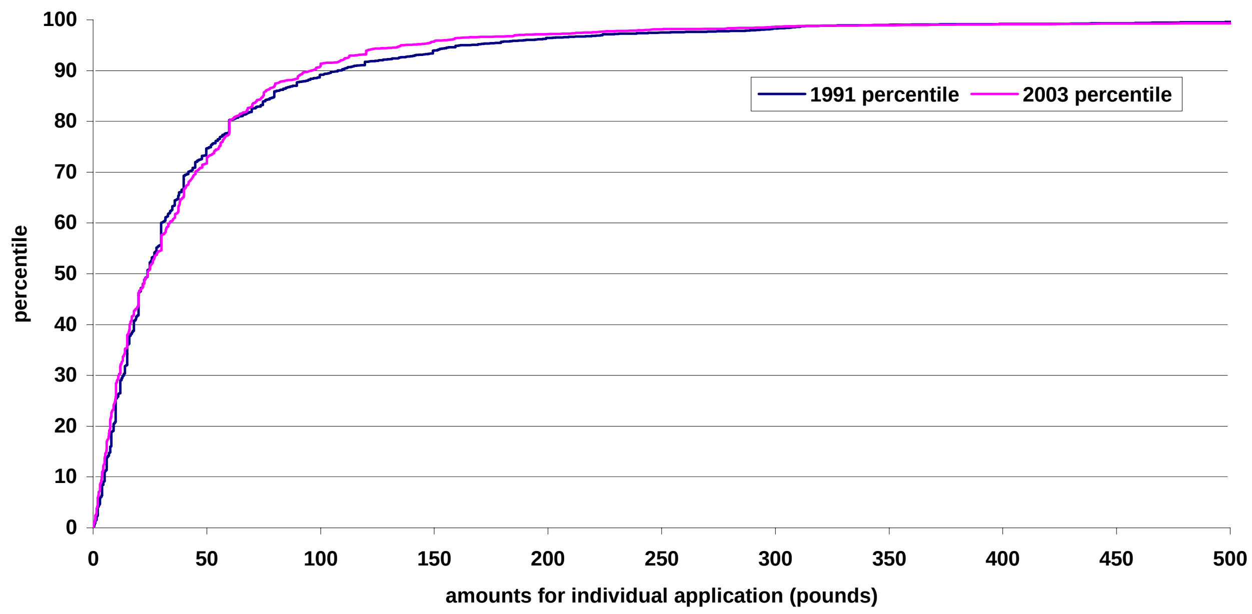
Figure 4. Methidathion use by commodity/site in 1991 and from 1994 through 2003 for commodities where ten-year average use exceeded 100,000 pounds (DPR PUR Database).



From Figure 5 it is evident that methidathion application amounts during 1991 was similar to that of 2003, though 1991 used a much higher total pounds. The table below summaries three percentile statistics and the corresponding methidathion pounds applied in 1991 and 2003

Percentile	Pounds used in 1991	Pounds used in 2003
50	23.3	24
90	107.6	96
95	163.3	135.45

Figure 5: Comparison of methidathion application amounts,1991 vs. 2003



From Figure 6 it is evident that the size of area (acres) treated for individual applications of methidathion during 1991 were similar to that of 2003, though in 1991 the total land area receiving methidathion was much higher. The table below summaries three percentile statistics and the corresponding methidathion applied acres in 1991 and 2003.

Percentile	Acres applied 1991	Acres applied 2003
50	18	20
90	88	75
95	150	96

Figure 6: Methidation use acres 1991 vs 2003

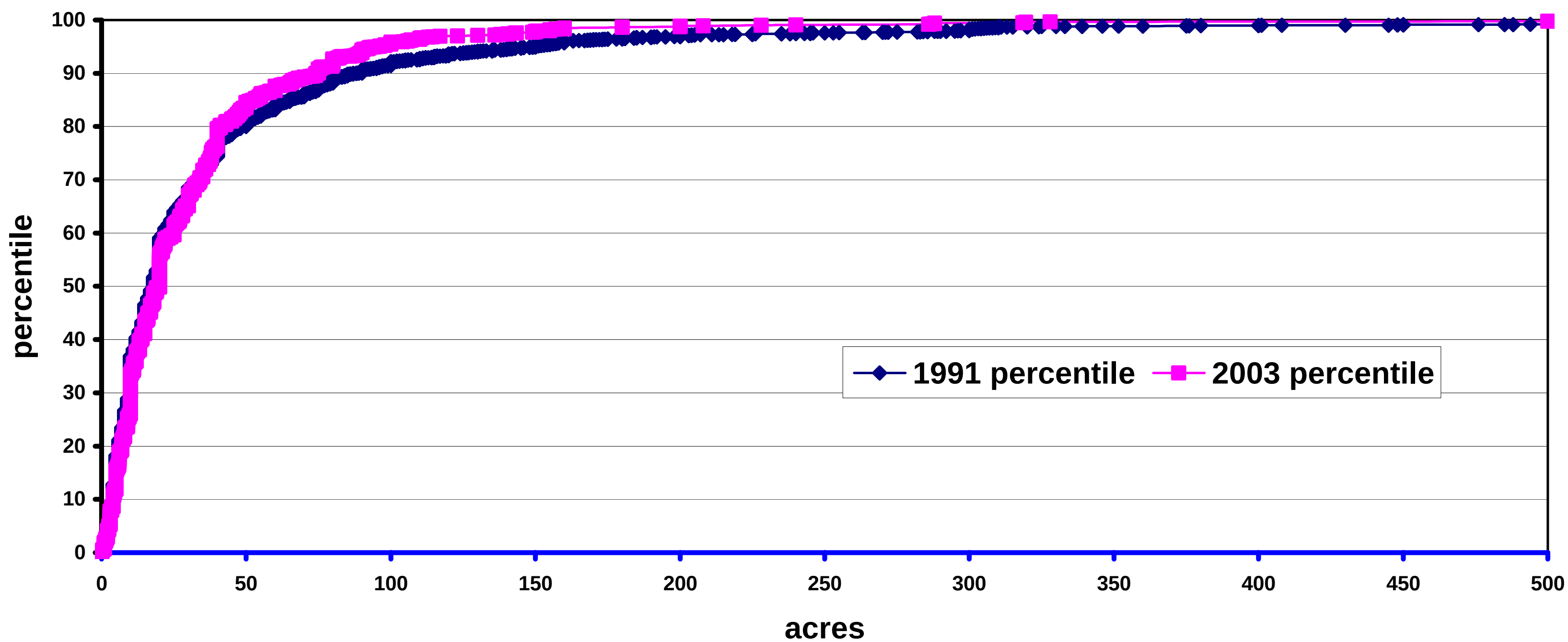
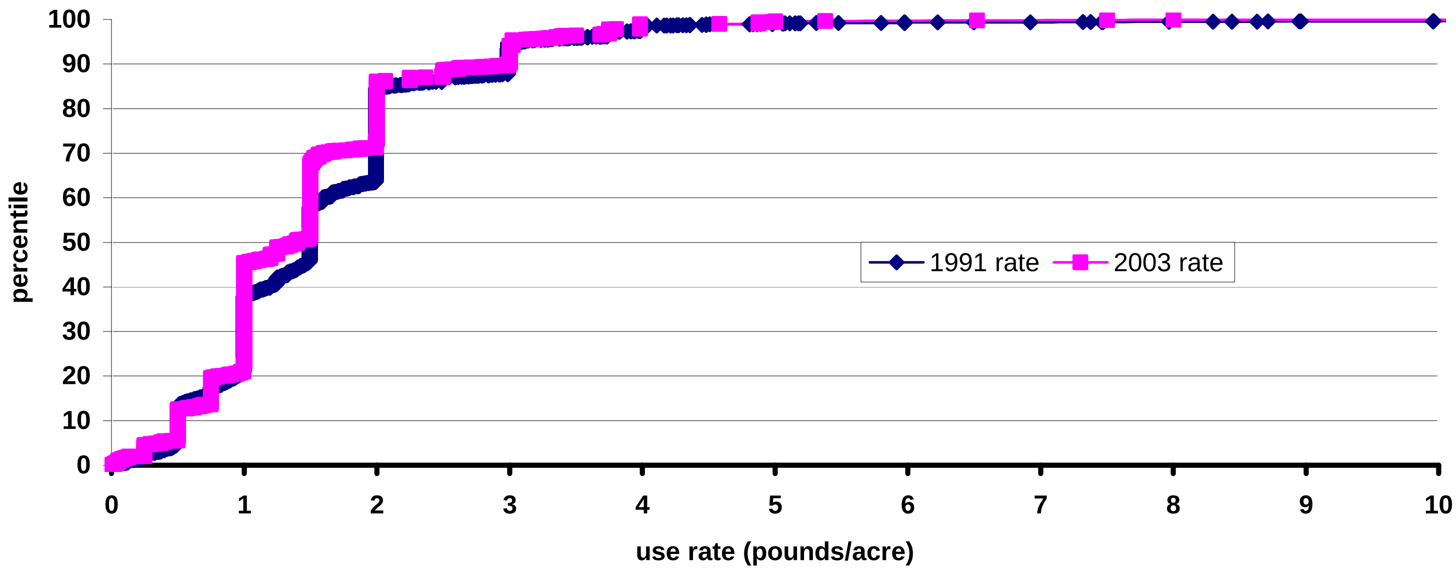


Figure 7 shows that methidathion use rates during 1991 were similar to that of 2003. The table below summarizes three percentile statistics and the corresponding methidathion use rates in 1991 and 2003

Percentile	Rate in 1991	Rate in 2003
50	1.49	1.4
90	2.99	3.0
95	3.08	3.02

Figure 7: Methidathion use rate 1991 vs 2003



Fate and Persistence in the Aquatic Environment

The chemical hydrolysis of methidathion in different aqueous media with pH values ranging from 1 to 10 was investigated (Burkhard, 1978). Rate constants and Arrhenius parameters were determined at 30, 50, and 70 °C (pH 1, 5, and 7) and 15, 30, and 50 °C (ph 9 and 10). Rate constants at 20 °C were also determined at pH 1, 5, 7, 9, and 10. Under the experimental conditions used, the rate of hydrolysis of methidathion was independent of the initial concentration. In acidic conditions, hydrolytic cleavage occurred primarily at the C-S bond. Under alkaline conditions, cleavage occurred at the P-S bond. Both intermediate hydrolysis products; the 4-(hydroxymethyl)- and the 4-(mercaptomethyl)-2-methoxy-1,3,4-thiadiazole-5(4H)-one, were unstable and decomposed rapidly to yield 2 methoxy-1,3,4-thiadiazole-5(4H)-one, the major degradate, in the alkaline as well as acidic hydrolysis of methidathion. In alkaline conditions, small amounts of a thioformic acid derivative were isolated. Assuming first order kinetics, calculated methidathion hydrolysis half-lives are summarized in Table 7.

Table 7. Methidathion hydrolysis half-lives (Burkhard, 1978).

Half-life, days	**Temperature, °C**	**pH**
41.3	20	1
10.0	30	1
0.8	50	1
0.08	70	1
33.8	20	5
9.0	30	5
0.63	50	5
0.08	70	5
40.8	20	7
10.1	30	7
0.83	50	7
0.09	70	7
25.5	15	9
12.3	20	9
3.1	30	9
0.25	50	9
2.8	15	10
1.9	20	10
0.54	30	10
0.05	50	10

An aqueous photolysis study was conducted in distilled water at 25 °C using a mercury arc rated 1900 $Jm^{-2}s^{-1}$ at 1.3 cm as the light source (Suter, 1983). The primary photodegradate was 2 methoxy-1,3,4-thiadiazole-5(4H)-one. The photolysis hale-life was 8.1 days. In another study, the aquatic photolysis half-life ($T_{1/2}$) was found to be 11 days at pH 7.0, and hydrolysis half-life ($T_{1/2}$) to vary from 37 days at pH 5, 48 days at pH 7 and 13 days at pH 9 (US EPA, 1999).

Methidathion has a low water solubility of 240 -250 mg/l at 20 ^{0}C. However, methidathion was detected in California surface water due to rain run-off from winter dormant spray. In a study on the distribution and mass loading of insecticides in San

Joaquin River, California, Ross et al., (1999) detected methidathion at a concentration of 0.08µg/l in one out of 18 samples analyzed for this pesticide. Ganapathy et al**.,** (1997) detected methidathion in 4 out of 222 samples (ranging from 0.061 to 0.22 ppb) that covered four California rivers; Sacramento river in November, 1993, Merced river in June, 1994, and Salinas and Russian Rivers in August, 1994. Nordmark et al**.,** in 1998, were able to detect methidathion in two sampling locations in the Sacramento river; 0.056 µg/l at Bryte, and 0.071 µg/l at Sutter Bypass, during the winter of 1996-1997. In 1996, Menconi and Siepmann reported the hazard assessment of the insecticide methidathion to aquatic organisms in the Sacramento-San Joaquin River System. In their study, the most acutely sensitive freshwater species tested was the cladoceran; *Ceriodalphina dubia* with a 96-h LC_{50} value of 2.2 µg/l. The most acutely sensitive saltwater species was mysid *Mysidopsis bahia* with a 96-h LC_{50} value of 0.7 µg/l. The lowest freshwater Maximum Acceptable Toxicant Concentration (MATC) was 0.83 µg/l for cladoceran *Daphnia magna*. The only available saltwater MATC was 0.04 µg/l for mysid *M. bahia*. Because of the lack of data, no Final Acute Values or Final Chronic Values were calculated to establish Water Quality Criteria for methidathion. From the reports it is evident that methidathion has been detected many times in Sacramento-San Joaquin River System. The highest concentration detected was 15.1 µg/l (Menconi and Siepmann., 1996). They cautioned that methidathion might present an acute and chronic hazard to aquatic organisms, particularly to sensitive aquatic invertebrate species such as cladocerans and mysid.

<u>Fate and Persistence in Soil</u>

The estimated adsorption and desorption co-efficients, though varying considerably, still show a pattern. The data summarized in Table 8 show the adsorption coefficients of methidathion estimated for different soils for a given organic matter content. The data were available for Adsorption Coefficient (K_d), Soil type, and % Organic matter (OM). K_{OC} values were calculated by using the formula $K_{OC} = K_d/OC \times 100$ where OC = OM/1.8. These coefficient values show considerable variability. However, the K_{OC} values for methidathion in different soil types suggest considerable leaching potential.

Table 8. Adsorption coefficients for several soil types in California**:** (DPR, 2005a).

Soil type	**[a]OC**	K_{oc}
Loam	0.7	415.7
Clay	2.8	310
Sandy	0.5	30.8
Sandy Loam	0.8	816
Sandy Loam	1.2	131.7
[a] = percent organic matter content		

Johnson, 1991 reported some of the important characteristics of pesticides to be considered potential lechers or non-lechers. The K_{OC} values, water solubility, half-life in moist soils, organic matter content and composition; all can influence the final outcome. Clayton, 2005., reported Methidathion to be a potential leacher. A study on field soil dissipation of methidathion applied to bare ground plots in Vero Beach, Florida, (DPR, 1986) to determine the stability and mobility in an Immokalee fine sand soil, the following was concluded. When this pesticide was applied at 4.0 lbs of active ingredient (a.i.) per acre, the detected methidathion concentrations in the 0-6” soil layer reached a maximum value of 1.6-1.8 ppm. The calculated first order half-life was 5 days. Methidathion residues were detected in 6-12” soil cores collected 0-7 days after application, and decreased to below the detection limit by 21 days after application. None was detected from any subsequent sampling depths. These results indicate that methidathion is not persistent in soil, and will not likely migrate below 12” in the field. The information submitted by the registrant, (DPR 1995a) shows that the most significant degradation pathway for methidathion in the environment is via microbial processes in the soil. The half-life in the aerobic soil is approximately 3 days. Anaerobic soil metabolism is also relatively rapid with a reported half-life of 30 days. Methidathion and its metabolites have a low mobility in soils. The compound is rapidly degraded in soil and in water by chemical, photolytic, and biological processes.

Artificial sunlight photodegredation of ^{14}C-methidathion on a sandy loam soil collected in Tulare County, California, was studied using a xenon lamp (DPR, 1989). The xenon lamp had a spectral energy distribution similar to that of natural sunlight. The intensity of the lamp was measured with a radiometer (4.25 nm bandwidth) from 290 to 750 nm at 10-nm wavelength intervals. The study did not indicate if wavelengths less that 290 nm were filtered. The degradation was found to be biphasic: an initial rapid rate of degradation, followed by a slower rate of degradation. The calculated photodegradation half-life of ^{14}C-methidathion for Phase 1 (Days 0-6) was equivalent to 8.96 days of natural sunlight. It took about 21.5 days of natural sunlight to complete Phase 2 (Days 6-17). Under dark conditions similarly labeled methidathion showed a half-life of 123.9 days. Under aerobic conditions ^{14}C-methidathion degraded rapidly from a value of 90.3% (Day-0) of the applied radioactivity to 7.6% by Day 11, and was not detectable by day 145. The calculated first order half-life was 3.1 days (DPR, 1990). Under anaerobic conditions ^{14}C-methidation degraded, and declined from a mean of 41.4% on Day-0 (anaerobic incubation) to 2.0% on Day-30 and to 0.6% on Day-62. The calculated half-life under anaerobic conditions was less than 30 days. When the soil was flooded, a substantial amount of radioactivity migrated from the soil into the water layer (DPR, 1990). In sterile soil samples, ^{14}C-methidathion had a half-life of 35.5 days (DPR, 1990).

Fate in Other Environments

Vorkamp et al. (2002) studied the fate of methidathion resides in biological waste during anaerobic digestion. They conducted three reactor experiments under various conditions of temperature, pH, and retention time. The influence of pH and temperature as well as the partitioning between solid and aqueous phases were studied in batch experiments. The mesophilic (25, 35 ^{0}C) reactor experiments showed a decline to about 10% of the maximum methidathion concentration within 30-80 days. In the thermophilic (55 ^{0}C) reactor experiment, methidathion disappeared within 20 days. The batch experiment showed an abiotic hydrolysis of methidathion over a period of 4 days, accelerated by alkaline conditions (pH 10.5 and 12.8) and high temperature (55 ^{0}C). The hydrolysis was also noticeable at a neutral pH, while methidathion was most stable at weakly acidic pH values. Methidathion bonded strongly to the biological waste, and the amount released into the water phase was below the maximum aqueous solubility. About 10 % of the methidathion remained non-extractable. They suspected co-sorption of methidathion to solid organic matter to be the reason. In a field soil dissipation study of methidathion, applied to alfalfa, in Fresno County, California, (DPR, 1986), the following was reported. The stability and mobility of methidathion and it's principal degredate [S-(2-methoxy-5-oxo-Δ^2 –1,3,4-thiadiazonil-4yl-methyl)-O,O-dimethyl-phosphorodithioate] in a Hanford fine sandy loam, when the pesticide was applied in a series of twelve applications, of 1.0 lb. a.i. per acre, the methidathion concentration in the first 0.6 inches of soil reached an average maximum value of 0.14 ppm; and the estimated initial soil half-life was eight days. The derivative was not found in any 0-6" or 6-12" soil cores. Although methidathion was detected in samples collected from a depth of 6-12" on the day of application, none was detected in any subsequent samples from this depth. This dissipation pattern suggests that the loss of methidathion in the 0-6" layer was not due to the downward migration of residues. The study concluded that when applied to an alfalfa stand in California, methidathion should not persist or accumulate in soil, and should not leach to lower soil depths.

Since methidathion is applied on many agricultural cops, it is important to examine whether this pesticide is detected in fruits, other commodities, including some processed products. Balaso et al**.** (2003) studying fifty samples of honey collected from local markets in Portugal and Spain during 2002, detected methidathion in 4% of the samples. In an investigation on degradation of pesticides that included methidathion in fortified red and white wine under conditions of light and darkness, Stavropoulos et al. (2001) followed their degradation for 80 days. They found that the half-life values of methidathion for white and red wine stored in diffuse daylight conditions were 20.1 and 20.0 days respectively. The half-lives for darkness were 21.1 and 24.2 days respectively. They concluded that photo-degradation does not play a role in decomposition of methidathion in wine under the study conditions. Kyriakidis et al. (2000) in a similar study investigated decomposition of methidathion sprayed on covered and uncovered grape vines. They sampled grapes 2 hours and 20 days after spraying, and stored either in a refrigerator, or left on the vine. They estimated the half-life of methidathion to be 5 days for uncovered vines and 7 days for covered vines, and 64 days for grapes stored in the refrigerator. Kyriakidis et al. in 2000, studied the effect of storage temperature and juice acidity on the degradation rate of methidathion in orange and peach juices. A known quantity of methidathion was added aseptically to these two juices and stored at 40, 15, and 0 ^{0}C, respectively. They found that refrigeration extended the half-life of methidathion beyond that of methidathion in the same juice samples stored at room temperature. The half-lives of methidathion in orange and peach fruit juices were; 330, and 385 days at 0 ^{0}C, 115 and 114 days at 15 ^{0}C, and 4.1 and 3.8 days, respectively, at 40 ^{0}C. A five-year monitoring survey was conducted in Japan (Akiyama et al., 2002) where they examined the presence of pesticide residues in a variety of agricultural products offered at the markets. They detected methidathion from local origin tomato, and from imported orange and grapefruit samples.

Fate and Persistence in the Atmosphere

When methidathion enters the atmosphere, it may be transformed and then removed through reactions with atmospheric radicals (OH and NO_3) and ozone (O_3). The potential for human exposure to methidathion and subsequent transformation products is therefore related to the rate of dispersion and potentially to the atmospheric lifetime and reaction rates for removal from the atmosphere. Although no data are available on the gas phase atmospheric chemistry of methidathion, literature data are available on the reactions of related organophosphorus compounds with O_3, OH, and NO_3. Studies conducted in environmental chambers have shown that atmospheric reactions of these compounds with O_3 and NO_3 are relatively unimportant. Reactions involving OH radicals, however, were found to be important with atmospheric lifetimes ranging from 0.8 hours to 2 days (Winer and Atkinson, 1990). Goodman et. al., (1988) investigated the Kinetics of the Atmospherically Important Gas-Phase Reactions of a Series of Trimethyl Phosphorothioates. One of the compounds studied; $(CH_3O)_2P(S)SCH_3$ is structurally very close to methidathion. For this compound they estimated a rate constant for reaction with OH radicals at room temperature of 5.5×10^{-11} cm^3 molecule $^{-1}s^{-1}$ and a calculated lifetime due to reaction with OH radicals of 5.0 hr for a 12-hr average OH radical concentration of 2.0×10^6 molecule cm^{-3}. The Estimation Programs Interface (EPI) Suite™ is a Windows® based series of physical/chemical property and environmental fate estimation models developed by the EPA's Office of Pollution Prevention and Toxic Substances, and Syracuse Research Corporation. AOPWIN™, an individual model in EPI Suite™, estimates the gas-phase reaction rate for the reaction between a chemical and OH, the most prevalent atmospheric oxidant (Meylan and Howard, 1993). The model also determines if NO_3 reaction will be important, and gas-phase O_3 reaction rates are estimated for olefins and acetylenes. Atmospheric half-lives are automatically calculated using assumed average OH and O_3 concentrations. AOPWIN™ used on methidathion resulted in an overall rate constant (k_{OH}) of 149.8×10^{-12} cm^3/molecule-sec, with a corresponding half-life of 0.071 day (12-hour day; 1.5×10^6 [OH]/cm^3). There were no structure matches in the model's experimental database. Atkinson et. al., (1989) examined the product formation from the gas-phase reactions of the OH radicals with $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$. The latter compound which was also studied in Goodman, et. al. (1988), and when reacting with OH radicals in daylight, the P=S bonds were oxidized to P=O bond containing products commonly known as oxons.

Aston and Seiber (1997) investigated airborne levels of methidathion and other organophosphates in the Sierra Nevada Mountains. In this study, residues of methidathion, and its oxon were detected in air (Table 9) as well as on pine needle samples.

Table 09: Concentration of methidathion and methidaoxon in air at study sites in California during summer of 1994 (adapted from Aston and Seiber, 1997).

Compound	**Laboratory Limits of Quantitation**	**Lindove elevation 114 meters.**	**Ash Mountain elevation 533 meters.**	**Kaweah elevation 1920 meters**
	pg/m^3	pg/m^3 range	pg/m^3 range	pg/m^3 range
Methidathion	85	15,000-400	230-[a]NQ	NQ
Methidaoxon	170	10,000-280	660-210	210-[b]ND

[a] NQ- not quantified.
[b] ND– not detected, (minimum detection limit: MDL 170 pg/m^3)

They found relatively high levels of methidathion and it's oxon at the site closest to Lindcove, CA, located in the Central Valley. At higher elevations, ambient air contained lesser amounts of parent pesticide. The derivative oxon form was more frequent relative to parent methidathion form at higher elevations. Pine needles from lower elevations contained small but detectable amount of both forms, but only the oxon form was detected at mid elevation. None was detected at the high elevation. They deduced that for airborne methidathion, foliar deposition is a significant summer fate process, along with atmospheric degradation and dilution.

The Air Resources Board, State of California, contracted a methidathion ambient and application-site air monitoring study in 1991, at the request of the Department of Pesticide Regulation, (Royce et al, 1993). Both ambient and application-site monitoring for methidathion and its more toxic oxidation product, methidaoxon, were performed in Tulare County, during June and July of 1991. The reason that the monitoring was done in this county was due to high use of methidation on citrus crops. Both methidathion and methidaoxon were detected at all five ambient monitoring sites and during the application-site monitoring study.

From Table10 and Table11, it is evident that both methidathion and methidaoxon were detected in ambient air at these sites during the study period. The maximum positive methidathion detection during this monitoring ranged from 0.07 µg/m^3 (5.6 ppt) to 0.56 µg/m^3 (45.2 ppt). More than 91 % of the total samples analyzed had no detectable residues (minimum detection limit = 0.03 µg/m^3; (2.42 ppt) for a 24 hour sample). The maximum detection for methidaoxon ranged from 0.092 µg/m^3 (7.42 ppt) to 0.10 µg/m^3 (8.87 ppt). Over 97 % of the total samples analyzed had no detectable residues (minimum detection limit = 0.09 µg/m^3; (7.26 ppt) for 24 hour sample).

Application-site monitoring for methidathion and methidaoxon was conducted in July 1991, for 48 hours after an application, in Tulare County (Tables12 & 13). Methidathion was applied by ground equipment at a rate of 1.5 pounds of a.i. per acre. Three sites were monitored. The samplers were situated approximately 25 yards north, 15 yards southeast, and 150 yards southeast of a 15 acre orange grove that received the methidathion application. Maximum positive methidathion detection from all sites ranged from 0.28 µg/m^3 (22.6 ppt) to 3.16 µg/m^3 (255 ppt). Almost 48 percent of the total samples analyzed had no detectable residues (minimum detection limit = 0.03 µg/m^3 (2.42 ppt) for a 24 hour sample). Maximum positive methidaoxon detections at each site ranged from 0.33 µg/m^3 (28.1 ppt) to 0.36 µg/m^3 (30.7 ppt). More than 76 percent of the total number of samples analyzed had no detectable residues (minimum detection limit = 0.09 µg/m^3 (7.26 ppt) for a 24 hour sample). This study also demonstrated that methidaoxon and methidathion could persist for extended periods of time near applications of methidathion. They suggested this reason as a possible explanation for the detection of this pesticide at the Air Resources Board monitoring site, located in an urban area (city of Visalia) and not in the immediate locale of known applications of methidathion.

Table 10. Summary of methidathion ambient air monitoring results in Tulare County. Samples (24-hour) were taken over a four-week period from June 27 to July 25, 1991. The Air monitoring station in Visalia was the background site (Royce et al., 1993).

Monitoring Site	**Highest** [a]**µg/m³**	**Positive** [b]**ppt**	**2nd Highest** **µg/m³**	**2nd Positive** **ppt**	**Mean Positive**[c] **µg/m³**	**Mean Positive**[c] **ppt**	**# of Samples**[d]	# Above [e]**EQL**
Sunnyside Union School, Strathmore	<EQL	<EQL	<EQL	<EQL	[f]NA	NA	17	0
Jefferson School, Lindsay	0.56	45.2	0.30	24.2	0.16	12.9	17	6
Exeter Union High School, Exeter	0.07	5.64	<EQL	<EQL	0.07	5.64	15	1
U.C. Lindcove Field Station, Exeter	<EQL	<EQL	<EQL	<EQL	NA	NA	15	0
Visalia	<EQL	<EQ	<EQ	<EQ	NA	NA	17	0
						Total	**81**	**7**

[a]micrograms per cubic meter

[b]parts per trillion

[c]mean of samples above the EQL

[d]field blanks and collocated samples excluded

[e]Estimated Quantitation Limit = 0.03 µg/m³ (2.42 ppt) for a 24-hour sample

[f]Not Applicable

Table 11. Summary of methidaoxon ambient air monitoring results in Tulare County. Samples (24-hour) were taken over a four-week period from June 27 through July 25, 1991. The Air monitoring station in Visalia was the background site (Royce et al, 1993) (adjusted to account for background values).

Monitoring Site	**Highest** [a]**μg/m³**	**Positive** [b]**ppt**	**2nd Highest μg/m³**	**Positive ppt**	**Mean μg/m³**	**Positive**[c] **ppt**	**# Samples**[d]	**# Above** [e]**EQL**
Sunnyside Union School, Strathmore	0.069	5.89	<EQL	<EQL	0.069	5.89	17	1
Jefferson School, Lindsay	0.077	6.58	<EQL	<EQL	0.097	8.29	17	3
Exeter Union High School, Exeter	<EQL	<EQL	<EQL	<EQL	[f]NA	NA	15	0
U.C. Lindcove Field Station, Exeter	<EQL	<EQL	<EQL	<EQL	NA	NA	15	0
Visalia	<EQL	<EQL	<EQL	<EQL	NA	NA	17	0
						Total	**81**	**4**

[a]micrograms per cubic meter

[b]parts per trillion

[c]mean of samples above the EQL

[d]field blanks and collocated samples excluded

[e]Estimated Quantitation Limit = 0.09 μg/m³ (7.26 ppt) for a 24-hour sample

[f]Not Applicable

Table 12. Summary of air monitoring results after an application of methidathion to an orange orchard (1.5 pounds of active ingredient per acre application rate). Samples were collected in Tulare County during July, 1991 before, during and for 48 hours after application (Royce et al., 1993).

				[a]µg/m³ (ppt)				
				Sampling Interval[b]				
Site	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Maximum Positive**
North	<EQL[c] (<EQL)	0.33 (26.6)	0.86 (69.3)	1.40 (113)	0.82 (66.1)	3.16 (255)	0.46 (37.1)	3.16 (255)
Southeast-1	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	1.25 (101)	0.60 (48.4)	0.30 (24.2)	1.25 (101)
Southeast-2	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.28 (22.6)	0.10 (8.06)	<EQL (<EQL)	0.28 (22.6)
Maximum Positive	<EQL (<EQL)	0.33 (26.6)	0.86 (69.3)	1.40 (113)	1.25 (101)	3.16 (255)	0.46 (37.1)	3.16 (255)

[a]micrograms per cubic meter and (parts per trillion)

[b] interval 1 =background on 7/10/91 from 1500-1600; interval 2 =during application on 7/10-11/91 from 2330-0900; interval 3 = 7/11/91 from 0900-1100; interval 4 = 7/11/91 from 1100-1500; interval 5 = 7/11/91 from 1500-2130; interval 6= 7/11-12/91 from 2130-0730; interval 7= 7/11-12/91 from 0730-0730;

[c] Estimated Quantitation Limit = 0.03 µg/m³ (2.42 ppt) for a 24-hour sample

Table 13. Summary of air monitoring results for methidaoxon after an application of methidathion to an orange orchard (2.99 pounds of active ingredient per acre application rate). Samples were collected in Tulare County during July, 1991 before, during and for up to 48 hours after application (Royce et al., 1993) (adjusted to account for background values).

				[a]µg/m³ (ppt)				
				Sampling	**Interval[b]**			**Maximum**
Site	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Positive**
North	<EQL[c] (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.31 (26.5)	0.24 (20.5)	0.21 (17.9)	0.31 (26.5)
Southeast-1	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.34 (29)	<EQL (<EQL)	0.13 (11.1)	0.34 (29)
Southeast-2	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)
Maximum Positive	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.34 (29)	0.24 (20.5)	0.21 (17.9)	0.34 (29)

[a]micrograms per cubic meter and (parts per trillion)

[b] interval 1 =background on 7/10/91 from 1500-1600; interval 2 =during application on 7/10-11/91 from 2330-0900; interval 3 = 7/11/91 from 0900-1100; interval 4 = 7/11/91 from 1100-1500; interval 5 = 7/11/91 from 1500-2130; interval 6= 7/11-12/91 from 2130-0730; interval 7= 7/11-12/91 from 0730-0730;

[c] Estimated Quantitation Limit = 0.09 µg/m³ (7.26 ppt) for a 24-hour sample

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